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Self-consistent electronic-band-structure calculation for Hg_3AsF_6

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The electronic structure of commensurate Hg_3AsF_6 is calculated using the self-consistent relativistic augmented-spherical-wave method. The results are compared with earlier pseudopotential calculations. The beat pattern as observed in the de Haas–van Alphen spectrum of $Hg_{3-\delta}AsF_6$ is interpreted as arising from the small spin-orbit interaction. The spin configuration of the electron states at the Fermi energy for the hypothetical commensurate structure is also reported.

I. INTRODUCTION

The problem of the electronic structure of incommensurate materials has recently received a great deal of attention.[1]. One material of continuing interest has been the incommensurate metal $Hg_{3-\delta}AsF_6$. The lattice of this material shows a rather unusual ordering.[2] A common thread is that the mercury atoms form linear chains which order at a temperature of 120–130 K.[3] The electronic band structure reflects the planar constant-energy surfaces characteristic of two interpenetrating quasi-one-dimensional metals. This behavior is complicated by the interchain couplings. Previous calculations of the electronic band structure have utilized a pseudopotential derived for elemental mercury.[4] It was assumed that the AsF_6 anions couple only weakly to the conduction-electron states near the Fermi level and their only effect is the lowering of the Fermi energy by binding the electrons near the bottom of the conduction band. This model was accurate enough to understand the topological features of the Fermi surface, and it was also able to interpret and predict the de Haas–van Alphen (dHvA) data. In this paper we consider an all-electron calculation which includes not only the effect of the Hg atoms but also the As and F atoms as well. In order to test the assumptions made in our previous work we have performed a self-consistent, fully relativistic augmented-spherical-wave (ASW) calculation on commensurate Hg_3AsF_6. The results of this calculation are reported here.

II. THE CRYSTAL STRUCTURE

By setting the incommensurability parameter (δ in $Hg_{3-\delta}AsF_6$) at zero we obtained a commensurate crystal on which band-structure techniques can be applied. The resulting structure is, besides the presence of the AsF_6 anions in this work, the same as used in the pseudopotential calculation of Buiting *et al.*[4] The unit cell as shown in Fig. 1 is body centered tetragonal (bct) and contains 40 atoms, so the primitive cell contains 20 atoms. The space group is $I4_1md$, which is nonsymmorphic. In Table I we list the inequivalent classes of atoms labeled by the type of atom and its Wyckoff position. In column 3 we give the coordinates of one of the atoms in each class; all other atomic positions in that class can be obtained by performing the group operations.

The vanishing of the δ parameter is obtained by expanding the tetragonal AsF_6 sublattice in the a and b directions, while keeping the distance between the mercury atoms inside the chains unchanged. This results in a lattice parameter (a) having the value 8.10 Å which is 7% larger than the observed value (7.45 Å).[2,3]

The increase of distance between the AsF_6 anions and thus indirectly the distance between anions and mercury atoms will of course influence the bonding between the fluorine and mercury atoms. Although we believe that this will hardly affect the states at the Fermi level, we di-

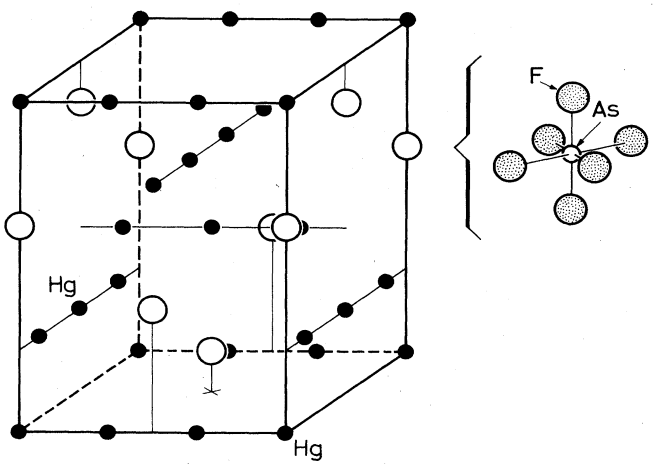

FIG. 1. The unit cell of Hg_3AsF_6. The crystal structure is bct ($a=8.01$ Å, $c=12.25$ Å) and has space group $I4_1md$. The open circles represent the AsF_6 octahedra.

TABLE I. Data on atomic and crystal parameters as used in the calculation. The coordinates are in units of a and c. The sphere-radii are given in angstroms. $\alpha=0.150$ (in units of c) and $\beta=0.162$ (in units of a). Lattice constants: $a=8.01$ Å, $c=12.25$ Å.

Element	Wyckoff position	Coordinate first atom	Number of atoms	Sphere radii	Atomic configuration
Hg	a	(0,0,0)	2	1.640	$6s\,6p\,5d$
Hg	b	$(0,\frac{1}{6},\frac{1}{4})$	4	1.640	$6s\,6p\,5d$
As	a	$(0,0,\frac{5}{8})$	2	0.635	$4s\,4p\,4d$
F	a	$(0,0,\frac{5}{8}+\alpha)$	2	1.830	$2s\,2p$
F	a	$(0,0,\frac{5}{8}-\alpha)$	2	1.830	$2s\,2p$
F	c	$(\beta,\beta,\frac{5}{8})$	8	1.743	$2s\,2p$

minished this effect by expanding the AsF_6 octahedra by 7% above the values given by Schultz *et al.*[2] (see Table I).

There are two quantities which are important for the properties of the conduction electrons: the spacing between the mercury atoms within the chains (=2.67 Å) and the spacing between the perpendicular chains ($=c/4$). The manipulations on the crystal structure as described above do not change these important quantities; they only alter the distance between parallel chains. However the coupling between the parallel chains is weak [less than 2 mRy (Ref. 4)], so this is just a minor effect. We can say that our adjustment of the crystal structure to obtain a commensurate crystal (i.e., $\delta=0$) has only a small energetic effect on the conduction states.

III. DETAILS AND RESULTS OF THE CALCULATION

We used the ASW method as described by Williams, Kübler, and Gelatt.[5] Scalar relativistic effects were included as described by Methfessel.[6] The ASW method employs a spherical approximation to the potential, which is comparable with the muffin-tin approximation in the Korringa-Kohn-Rostoker method. These kinds of approximations can lead to inaccuracies in the case of lower-dimensional structures. The lowest-order term which is neglected in the spherical harmonic decomposition is the $l=1$ term. This term will not couple with s states on mercury but can have an influence on the mercury p states. The wave-function character of the states around the Fermi energy are almost exclusively of mercury s type. Hence we do expect an appreciable influence of spherical approximations on the Fermi-surface properties. However, the precise value of the gap between s and p states on mercury has to be interpreted with care. The basis set included s, p, and d functions on all sites, except for the fluorine sites, which includes s and p functions only (see Table I). The internal summation for the three-center terms was carried out to one l value higher than was included in the basis set: up to $l=3$ for all sites except for fluorine, where the summation was truncated at $l=2$. The sphere radii were chosen in such a way that the overlap between the various Wigner-Seitz spheres was well balanced. The sphere radii are given in Table I. Self-consistency was achieved in about 30 iterations to a precision of $1:10^{-4}$. Hereafter the obtained potentials were used for a calculation including the spin-orbit interaction. This was done by inserting the $\mathbf{L}\cdot\mathbf{S}$ operator directly into the ASW formalism. The resultant secular matrix was of rank 240. The values of the spin-orbit coupling parameters were derived from spectroscopic data[7] rather than being calculated from the gradient of the potential.

The obtained band structure is shown in Fig. 2 along the high-symmetry lines. There are 156 filled valence states of primarily mercury d and fluorine s and p character below the panel of Fig. 2, which have been omitted for visual clarity. The bands shown are primarily of mercury s and p character. The present band structure is similar to a previous one calculated using the pseudopotential method.[4] There are a few differences between the two calculations. The gap between the bottom of the mercury $6p$ band and the top of the $6s$ band is small, about 25 mRy (Fig. 2). In the pseudopotential calculation the gap is somewhat larger, namely, about 80 mRy. This indicates that the effect of the discrete, atomic nature of the mercury chains is weak and the approximation of the chains by tubes is rather good.[8,9] Another difference is that the states at Z, namely, Z_1, Z_2, and Z_5, are separated by about 65 mRy; in the pseudopotential calculation these states are almost degenerate. At Γ, the Γ_5 state at 470 mRy falls nearly in the middle between the Γ_1 state at 570 mRy and the Γ_2 at 370 mRy. In the pseudopotential calculation the Γ_5 state is higher than the center of gravity of the Γ_1 and Γ_2 states. These differences indicate that the difference in Madelung energies between different

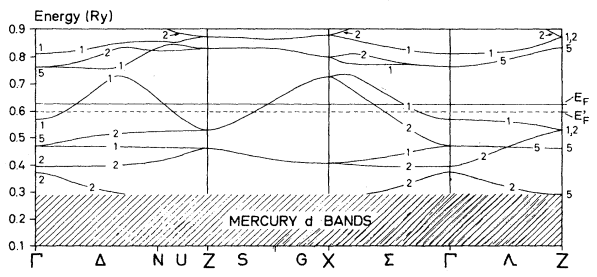

FIG. 2. The band structure along the symmetry lines for bands 157–175. The dashed region indicates the "sea" of flat mercury d bands, which we left out for reasons of clarity. Note the twofold degenerate (without spin) bands along the Z to X line. No bands cross the Fermi level in the Λ direction, indicating low conductivity in the c direction.

sites along the chain is very small (less than 10 mRy). The pseudopotential calculation gave a large difference in Madelung energies ($\approx$50 mRy), since it ignored the anions, and thus only the positively-charged mercury atoms contributed to the Madelung energy. The ASW calculation shows that the anions cancel to large extent the variation of Madelung energy along the chains caused by the cations, and therefore the motion of the conduction electrons along the chains is nearly free. Thus the ASW calculation shows that the "tube potential"[8] is an excellent approximation to the real potential.

E_F (Fig. 2) is the Fermi energy calculated for the commensurate structure Hg_3AsF_6. For the real incommensurate structure $Hg_{3-\delta}AsF_6$, we change the Fermi energy to E_F' to account for the slightly smaller occupation of electrons on the mercury atoms. The Fermi surface as obtained from the ASW calculation is similar as the one obtained from the pseudopotential,[4,8] and in accord with the dHvA experiment.[10,11] However, it will be modified slightly by the spin-orbit interaction as is described in the next section.

The density of states for the energy range in the vicinity of the Fermi level is displayed in Fig. 3. The shape of the curve reflects the low dimensionality of this system. The part between 0.39 and 0.47 Ry clearly results from the one-dimensional character of the conduction states, while the nearly constant density of states near the Fermi level is characteristic of two-dimensional systems. The density of states at the Fermi energy is small ($\approx$12 states/Ry cell). As a result the electronic contribution to the specific heat at low temperatures is small also.[12]

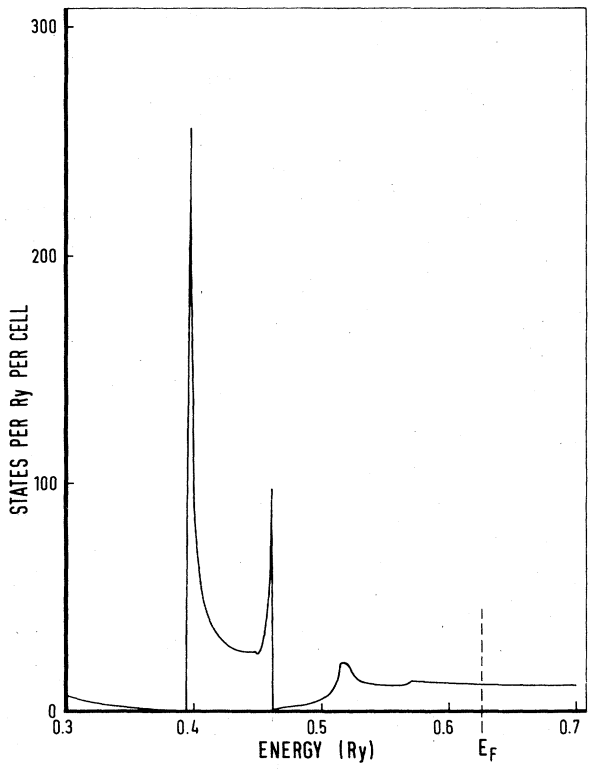

FIG. 3. The density of states of commensurate Hg_3AsF_6. It reflects the one- and two-dimensional character.

IV. SPIN-ORBIT INTERACTION

One of the features that our (artificial) structure and the observed incommensurate structure have in common is the lack of inversion symmetry. The consequence of this is that for a general **k** point spin-up and spin-down states do not belong to the same two-dimensional representation any more, i.e., they can split up in two singlet states. (The Kramers degeneracy, due to time inversion, is between Bloch states $|+\mathbf{k}\uparrow\rangle$ and $|-\mathbf{k}\downarrow\rangle$.) The splitting at the Fermi level is rather small because of the s character of the conduction electrons ($\approx$2–6 mRy), but it has a rather remarkable effect on the Fermi surface sheets as is shown in an exaggerated scale in Fig. 4. Every dHvA orbit is intrinsically split (even in zero magnetic field) and will give rise to dHvA signals slightly differing in frequency. Especially for the ϵ orbit—since this is the biggest orbit—this difference in area will be most pronounced. For this orbit van Deursen *et al.*[11] observed a beat pattern on the ϵ signal with a period of 6.3 T which is smaller, but comparable to, the difference that we calculated (25 T).

In Fig. 4 we have also indicated for certain points on the Fermi surface the direction of the electron spin (actually the expectation value $\langle\sigma\rangle$). For the $k_z=0$ plane, as shown in Fig. 4, all the spins lie in the x-y plane, perpendicular to the group-velocity vector, as might have been expected by dynamical considerations. The vanishing of $\langle\sigma_z\rangle$ can be understood from the fact that the only possible electronic movement away from the chains is in the z direction, i.e., a jump to a neighboring (perpendicular) chain. The coupling of the spin to such an orbital motion will result in a favorite spin direction, not along the z direction. On special lines such as Γ to X and Γ to Z, the spin directions shown in Fig. 4 are a natural consequence of the group symmetry. For example, the glide plane $(\bar{y},\frac{1}{2}+x,\frac{1}{4}+z)$ and mirror plane $(\bar{x},y,z)$, contained in $I4_1md$, confine the expectation value $\langle\sigma\rangle$ to be strictly perpendicular to the mirror-planes considered.

The lack of inversion symmetry is essential for the spin-spin Fermi surface. The "tube-potential," used by Buiting *et al.*[8] has the space group $I4_1/amd$ which does possess a center of inversion, therefore the spin states at a general **k** point are degenerate. The incommensurate structure can be seen as having approximate inversion symmetry, when a very large cluster is considered; however, on a scale of a unit cell, there is no inversion symmetry. This means that locally, where the arrangement of chains is somewhat similar to that in Fig. 1, the spin states are split, but globally they are not, since spin splittings in different regions cancel out. We can say that the spin sees an orbital field that varies in space due to the incommensurability. Because of the large value of v_F, the spin has no time to align itself along the orbital field. However, the rapidly fluctuation orbital field can have drastic effects on spin relaxation, it can perhaps induce spin-density-wave states, it can drastically affect superconducting properties, etc. Thus the arrows of Fig. 4 in

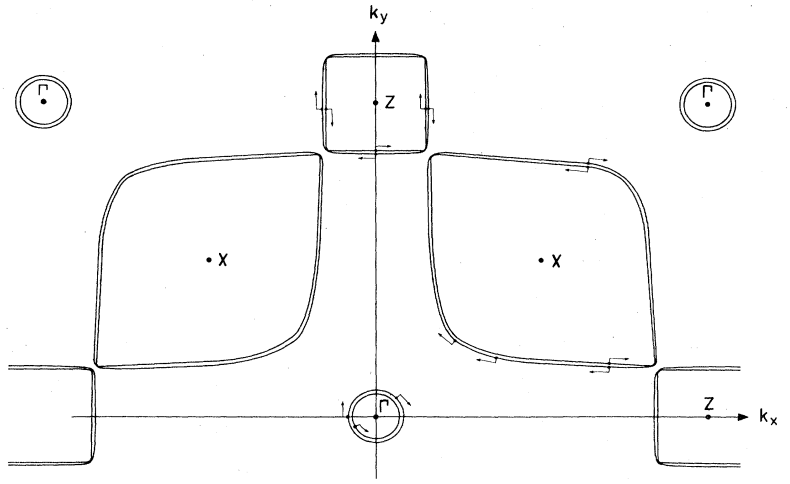

FIG. 4. The cross section of the Fermi surface in the $k_z=0$ plane. Each spin degenerate state at the Fermi surface is split due to spin-orbit interaction and lack of inversion symmetry. The splitting as shown is enlarged by a factor of 200. The arrows indicate the direction of the electron spin.

effect give the value of the orbital field, seen by the spins, rather than the spin direction *per se*.

The zero-field splitting between the two spin states (at a given **k**) is equivalent to the Zeeman splitting caused by a field of about 100 T. NMR relaxation time measurements[13] indicated that the Zeeman precession is slow compared with the cyclotron frequency. The present calculation suggests that external fields (of a few tesla) indeed have a negligible effect on the spin. The difference that we calculate here for the unit cell, for which the breakdown of inversion symmetry is maximal, is 25 T. Thus, it is possible that the beat pattern observed in the dHvA experiment is indeed due to the spin-orbit coupling, but more work has to be done to understand the effects of modulation of the spin-orbit coupling due to the incommensurability.

V. CONCLUSIONS

The calculations reported here show that the conclusions drawn from the pseudopotential calculation of Buiting *et al.*[4] are correct. The conduction electrons are tightly bound to the mercury chains while they can move freely along the chains. The interchain coupling is about 100 mRy, which is large but not large enough to enable appreciable conduction in the *c* direction. The gap between the mercury *s* and *p* bands is in this work about a factor of 3 smaller than in the pseudopotential calculation. This means that the effect of the discreteness of the mercury atomic positions is even weaker compared with our previous findings. This result strengthens the models which approximate the potential of the mercury chains atoms by a structureless cylinder.[8,9] It also confirms the conclusions of Buiting *et al.*,[8] who found that the effect of incommensurability due to the discrete nature of the mercury atoms is weak (of the order of a few mRy).

The effect of the spin-orbit interaction on the states near the Fermi level is weak as can be expected for states having mainly *s* character and an essentially one-dimensional electronic structure. However, in combination with the lack of inversion symmetry the influence of the spin-orbit interaction on the Fermi surface is important. For the incommensurate crystal it splits the Fermi-surface sheets, which are spin degenerate in the nonrelativistic case, into two nondegenerate sheets on a local scale. The result of this phenomenon is apparently observed in the experiments such as the de Haas–van Alphen effect and nuclear magnetic resonance. The exotic structure of this system causes the electron spin to lie in the *x*,*y* plane.

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